Alignment of nematic liquid crystals on mixed Langmuir-Blodgett mono-layers

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Abstract

Mono-layers of stearic and behenic acids and mixtures of them in different proportions, deposited with the Langmuir-Blodgett (LB) technique, were used to study the alignment and the alignment dynamics in nematic liquid crystal cells. A relaxation process from a splay-bend flow induced metastable orientation to the homeotropic one occurs. The lifetime of the metastable state was found to depend on the mono-layer composition. The transition between the homeotropic and the conical anchoring was found to be irreversible in the case of the mixed aligning mono-layers: on cooling from the isotropic phase a quasi-planar nematic state (schlieren texture) appears. It is stable in a range of a few degrees below the clearing point and, on decreasing the temperature, relaxes to the homeotropic state in form of expanding domains.

Keywords: Langmuir-Blodgett mono-layers, mixed mono-layers, nematic liquid crystal, homeotropic alignment, anchoring.

Introduction

The Langmuir-Blodgett (LB) technique enables the deposition of organic aligning films with controlled molecular order and thickness similar to but much thinner that those often used as aligning films in liquid crystals cells. They allow a very good homeotropic alignment over large areas.

Recently [1] we have shown that for pure stearic (C18) and behenic (C22) aligning mono-layers during the process of filling of the cell the nematic liquid crystal (NLC) molecules are preferably aligned along the filling direction: the molecules in the centre of the cell gap are essentially parallel to the substrate and a splay-bend deformation in the NLC molecules is induced by the presence of the aligning layer (see Figure 3). As soon as the flow stops on complete filling, domains of homeotropic alignment nucleate at the edges of the cell and continuously grow until the whole sample becomes homeotropic. The relaxation of the splay-bend deformation into the homeotropic state is partially a result of the elastic relaxation of the splay-bend deformation, but seems to have a contribution also from the LB film itself which is distorted by the flow and

relaxes to the equilibrium state, where the mono-layer molecules are in the upright position. Since the lifetime of the splay-bend state was found to be very similar for C18 and C22, depending only on the cell thickness, the rôle of the LB mono-layers in the process is much less pronounced than that of the liquid crystal.

In this work mixed C18/C22 mono-layers were used for investigating the alignment dynamics in nematic liquid crystal cells. The alignment was studied during the filling process and pursued during the relaxation to the equilibrium state. The temperature stability of this state was also investigated.

Experiment

1 mM solutions of stearic, behenic, or stearic/behenic mixtures in Merk chloroform were spread onto the surface of ultrapure Milli-Q water in a LB trough. Then the mono-layers were compressed at a rate of 0.3×10^{-3} ($\mathrm{nm}^2\mathrm{s}^{-1}\mathrm{molecule}^{-1}$) until the desired pressure was reached.

We used indium tin oxide (ITO) coated glasses as substrates. They were first cleaned [1] and then immersed in the sub-phase before spreading the mono-layer. The transfer onto the glass occurred during the extraction of the glass from the sub-phase (10 mm/min).

The glass plates were cut and assembled in sandwitch cells spaced with 15 μm polyester films supplied by Milar. Care was taken do not touch, and thus contaminate, the inside surface of the cells.

The cells were capillary filled with MBBA (Aldrich) at room temperature. The observations on them were made with a polarizing microscope in orthoscopic as well as conoscopic regime with the sample insered in a hot stage between crossed polarizers. The microscope was also equipped with a videocamera connected to a computer.

Results

Isotherms

In Figure 1 the surface pressure versus molecular area isotherms for films of pure stearic acid (C18), pure behenic acid (C22), and a number of C18/C22 mixtures with different C18:C22 ratios are shown.

To quantitatively study the molecular arrengement of the mixed C18/C22 mono-layers we followed Gaines [2]. Mono-layers in which the components are immiscible may be thought as made up of two separate mono-layers in equilibrium with each other. The area of the film will be the sum of the areas of the separate films, or

$$A_{12} = N_1 A_1 + N_2 A_2, \tag{1}$$

where A_{12} is the mean molecular area of the two-component film, A_1 and A_2 are the molecular areas of the two single component films at the same surface pressure, and N_1 and N_2 are the mole fractions of the two components. Any deviation from (1), also called "line of no interaction", provides evidence of miscibility as well as some sort of molecular interaction in the film [2].

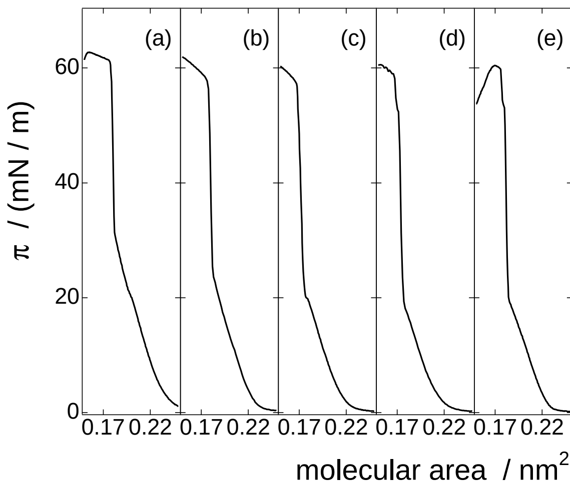
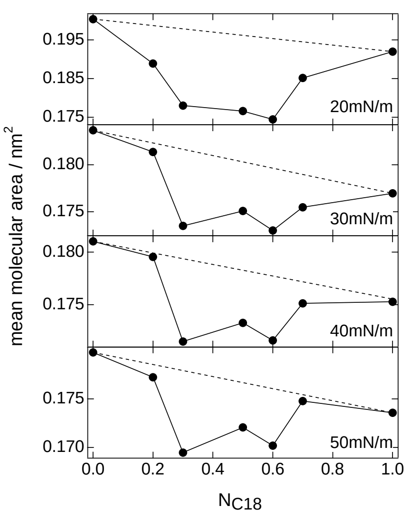
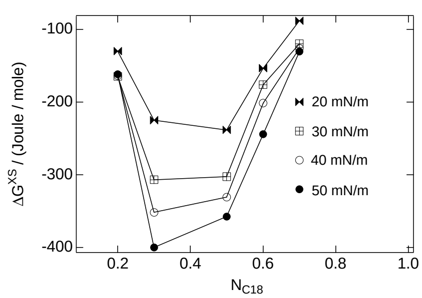


Figure 1: Surface pressure versus area per molecule isotherms for stearic/behenic acid mixtures. (a) 0:100, (b) 20:80, (c) 30:70, (d) 50:50, (e) 60:40, (f) 70:30, (g) 100:0.



(a)



(b)

Figure 2: (a) Average molecular area of the LB film as a function of the molar fraction of C18. The dashed line is the "line of no interaction" and the dots are the experimental values. The fact that all the experimental points lie below the "line of no interaction" indicates that the two compounds mix [3,4]. (b) Excess free energy of mixing calculated from the isotherms in Figure 1 as a function of the molar fraction of C18 for four different values of the π^* pressure (cfr. eqn.(2)). The values are all negative indicating that C18 and C22 mix.

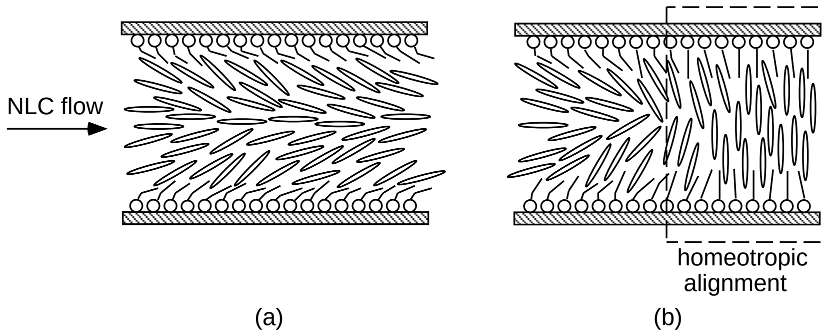


Figure 3: (a) During filling the LB mono-layer seems to be strongly influenced by the flow with the chains distorted in the filling direction. A splay-bend deformation is induced in the NLC by the flow. (b) When the flow stops the LB film and the splay-bend deformed liquid crystal both contribute to the relaxation towards the homeotropic state [1].

In Figure 2(a) the mean molecular area in the mixed film is plotted versus the mole fraction of C18 for four different surface pressures. In the figure the dashed line represents the "line of no interaction ", and the dots are the experimental values. The fact that all the experimental points lie below the line of not interaction indicates that the two components mix [3, 4].

Once we established that the components of the mono-layer have a tendency to mix we may also calculate the excess free energy of mixing for a given surface pressure π^* [2],

$$\Delta G_{\mathrm{xs}} = \int_0^{\pi^*} (A_{12} - N_1 A_1 - N_2 A_2) d\pi, \tag{2}$$

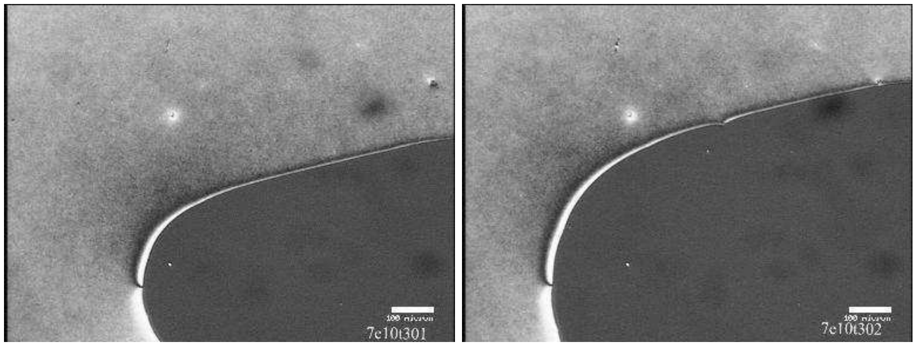
which can be done directly from the $\pi - A$ curves of the pure and the mixed mono-layers. For a truly mixed mono-layer ΔG_{xs} must be negative. In Figure 2(b) ΔG_{xs} is plotted as a function of the C18 fraction for four different surface pressures. The values of the excess free energy of mixing are all negative, confirming the already observed tendency of the two components to mix.

Alignment

The cells were capillary filled with MBBA at room temperature (where MBBA is in the nematic phase). As we have shown [1], during filling the chains of the molecules constituting the LB film are distorted by the flow and a splay-bend deformation is induced in the NLC. As soon as the flow stops the distorted LB film and the splay-bend deformed liquid crystal both contribute to the relaxation towards the homeotropic state.

An example of how the homeotropic domains expand in the cell is given in Figure 4.

We measured the speed with which the homeotropic domains expand in the cells taking pictures at fixed time intervals for the different aligning layers. The speeds were calculated as the area covered by the front of a homeotropic domain in a certain time interval, divided by the length of the front and the time interval. The results are shown in Figure 5. The fact that the lifetime of



(a) (b)

Figure 4: Cell between crossed polarisers. The LB aligning film is a C18:C22 50:50 mono-layer; the thickness of the cell is 15.2 μm. The cell is completely filled with MBBA, the NLC flow has ceased, and the homeotropic domains (dark) expand in the quasi-planar domain (light). The two pictures were taken with a time interval of 20 s.

Table 1: Alignment obtained for the different compositions of the LB mono-layers.

LB film composition	Alignment
C18:C22 0:100	Not well defined
C18:C22 20:80	Not very good homeotropic
C18:C22 30:80	Good homeotropic
C18:C22 50:50	Very good homeotropic
C18:C22 60:40	Very good homeotropic
C18:C22 70:30	Good homeotropic
C18:C22 100:0	Good homeotropic

the splay-bend state depends on the mono-layer composition indicates that that the relaxation process is not only due to the deformed liquid crystal, but also to the LB film.

The quality of the homeotropic alignment was studied by conoscopy. For a uniaxial compound ordelly oriented with the c-axis perpendicular to the glass plates, the conoscopic figure should consist of a black cross in a white background [5]. In Figure 6 the conoscopic figure of a sample with C18:C22 50:50 aligning layer is shown. In Table 1 the results of the conoscopy for all the different aligning layers are summarised.

From Figure 5 and Table 1 we observe a connection between the quality of the homeotropic alignment and the speed of expansion of the homeotropic domains: for the higher speeds we also have the best alignment. Indeed, the higher speed implies a stronger anchoring which in turn gives a better alignment. We also observe that in general mono-layers containing a high fraction of C18 give a better alignment. The alignment given by C22 is not very well defined, but the

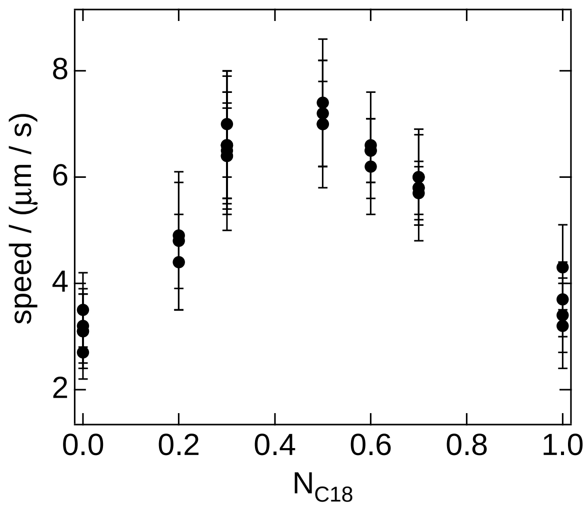


Figure 5: Speed of expansion of the homeotropic domains as a function of the C18 fraction in the aligning mono-layer. The cell thickness is about 15 μm. The homeotropic domains expand faster for the mixed aligning mono-layers than for the pure ones. The composition C18:C22 50:50 gives the highest speed which decreases on increasing the quantity of one or the other fatty acid.

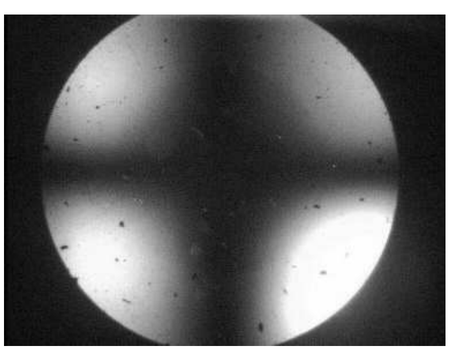


Figure 6: Conoscopic figure of a cell with C18:C22 50:50 aligning layer. The cell is 15 μm thick. The homeotropic alignment is very good.

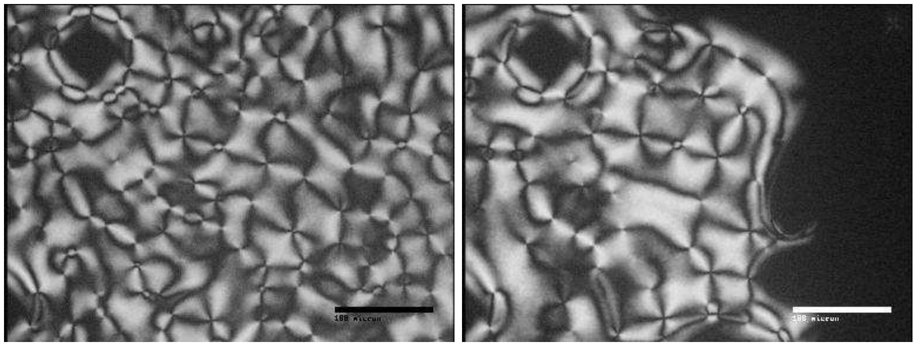


Figure 7: Cell between crossed polarizers. The aligning layer is C18/C22 20:80. (a) On cooling from the isotropic phase, just below the clearing point, we see a calssical schlieren texture [8], as if we there were no aligning layer. (b) 5°C below the clearing point. The homeotropic alignment appears in domains (dark) which extend to the whole cell.

addition of a small fraction of C18 gives already a homeotropic alignment, even thoug not very good. Increasing the quantity of C18 the homeotropic alignment improves and reaches the best quality for the C18:C22 ratios of 50:50 (Figure 6) and 60:40. Also, the pure C18 mono-layers gives a good homeotropic alignment.

Anchoring transition

On heating, we observed a first-order anchoring transition [1,6] in a very narrow temperature range, just below the clearing point. At the transition a set of bright circular domains with dark crosses appear in the sample; at constant temperature, they grow and coalesce, forming larger domains. The appereance of these domains between crossed polarisers is consistent with a degenerated tilted orientation of the NLC molecules, or conical anchoring, also expected in the case of LB aligning films [7].

On cooling from the isotropic phase the transition to the nematic homeotropic phase is different for the pure and the mixed mono-layers. For the pure C18 and C22 mono-layers the bright domains appear again and the transition to the homeotropic phase takes place inside the domains [1, 6]. For all the mixed C18/C22 mono-layers, on cooling from the isotropic phase, a nematic, non-homeotropic phase appears just below the clearing point (see Figure7(a)). It resembles the classical nematic phase in a cell without aligning mono-layer: it is characterised by domains were the director points in different directions (schlieren textures [8]) and it is stable in a temperature range of ca. 5°C below the clearing point. On further cooling, domains with homeotropic alignment appear in the sample and quickly expand until the whole sample becomes homeotropic (see Figure 7(b)).

A possible explanation for the different behaviour at the isotropic to nematic phase transition is shown schematically in Figure 8 [9]. The portion of the behenic acid molecules above the height of the adjacent stearic acid molecules will exhibit thermal motion which increases as the temperature increases. The phase transition from nematic to isotropic is not much affected by this thermal

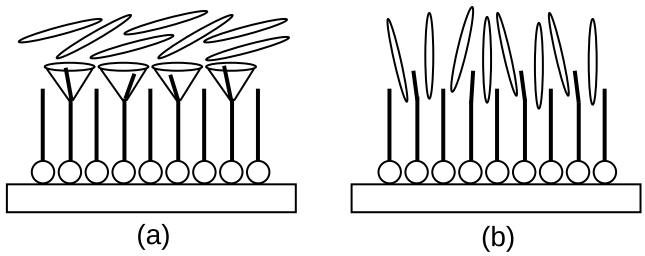


Figure 8: Schematic view of the thermal motion of the upper segments of the aliphatic chains [9]. (a) Just below the clearing point the thermal motion is large. The cones represent the time-average space occupied by the thermal motion of the segments. In this situation there is not space for the liquid crystal molecules to penetrate into the layer of the chains. (b) More than 5°C below the clearing point. Now the space occupied by the chais in thermal motion is small enough to let the liquid crystal molecules penetrate into the layer of the chains.

motion, being a transition from an ordered state to a totally disordered one: the thermal motion is in this case a help rather than an impediment. On the contrary, at the phase transition from isotropic to nematic, this motion prevents the recovering of the homeotropic alignment because the upper segments of the chains in motion occupy the space necessary for the liquid crystal molecules to penetrate into the layer of the chains. In this situation we have the nematic phase of the liquid crystal but not the homeotropic alignment (Figure 8(a)): the schlieren texture will appear in the sample (see Figure 7(a)) because the LB film does not supply any preferred direction of alignment. On cooling, the thermal fluctuations of the segments decrease and the liquid crystal molecules can penetrate into the layers of the chains and restore the homeotropic alignment, as shown in Figure 8(b).

Conclusions

Alignment dynamics and properties of nematic liquid crystals on pure and mixed stearic/behenic acids Langmuir-Blodgett mono-layers have been investigated. Mono-layers with a high C18 fraction give a good homeotropic alignment. Increasing the fraction of C22 the alignment deteriorates and for pure C22 there is no well defined alignment at all in the cells. The speed of the relaxation process from the splay-bend flow-induced orientation to the homeotropic state, as well as the quality of the homeotropic alignment, were found to depend on the composition of the LB film. They are also correlated, because a faster relaxation implies a stronger anchoring energy, which in turns gives a better alignment. This has been also found in our experiment.

From the results we can conclude that the LB films participate in the relaxation process in accordance with a model in which the chains are mobile and can be deformed by the LC flow: once the flow has ceased, the chains relax to their equilibrium state with a speed which depends on the mono-layer composition. In the equilibrium state the chains are in the upright position and move only because of thermal fluctuations. At room temperature these fluctuations do not

disturb the homeotropic alignment, but in the case of mixed mono-layers on cooling from the isotropic phase they prevent the transition from the isotropic directly to the nematic-homeotropic phase. In fact, since the chains have different lengths, the upper segments of the longest chains undergo strong fluctuations and do not leave space for the liquid crystal molecules to penetrate into the LB layer.

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